TECHNOLOGY DEVELOPMENT DATA SHEET



A Continuous Emission Monitor for Toxic Metals in the Off-Gases of Thermal Treatment Facilities



Developer: Laser Diagnostics LLC

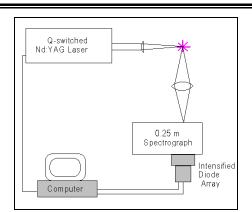
Contract Number: DE-AC21-96MC32194

Crosscutting Area: CMST

Problem:

Environmental regulations and public concerns are drastically limiting thermal treatment options, such as incineration, for disposal of solid waste materials contaminated with toxic metals. Current Clean Air Act Amendments (CAAA) limit the release of toxic metals into the atmosphere and intermittent sampling is required to demonstrate compliance. However, the U.S. Environmental Protection Agency (EPA) is considering altering the present emission limits for toxic metals and requiring continuous emission monitoring (CEM) to immediately warn of an accidental introduction of toxic metals into the atmosphere.

Use of standard laboratory analysis techniques would not give true continuous, real-time analysis. Operators of thermal treatment facilities need a continuous, real-time method of monitoring the off-gases for toxic metals. Ideally, this method would feature low maintenance costs, automated sampling and analysis procedure, and sufficient sensitivity to ensure compliance with EPA and other regulations for all the CAAA regulated metals.



Solution:

Develop laser induced breakdown spectroscopy (LIBS), an in situ instrumental method with the required sensitivity to perform continuous elemental analysis for toxic metals in off-gases. Several potential methods include X-ray fluorescence (XRF), inductively coupled plasma, atomic emission spectrometry (ICP-AES), and LIBS.

Of these methods, LIBS is the only one that performs the analysis in situ - offering the distinct advantage of not having to pull samples from the gas stream.

In situ sampling also offers the fastest response time, which is important for a CEM designed to warn of an acute toxic metal release giving thermal treatment operators

time to respond to dangerous levels of toxic metals being released into the atmosphere.

Benefits:

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- Continuous monitoring of the offgases from thermal treatment facilities for release of dangerous levels of toxic metals
- Reduced overhead costs compared to traditional gas sampling with laboratory analysis
- Sampling point in the gas stream can be adjusted with optical techniques
- ►Portable systems could be used at many sites to compare toxic metal levels to that expected from feed stock contents and observe fluctuations in levels

Technology:

LIBS is demonstrated by focusing a pulsed laser in a gas or on a solid surface. With a pulse energy and peak power above a given threshold, which depends on the medium and the laser beam quality, an electrical breakdown occurs. This breakdown causes the formation of a pinpoint of plasma in which everything is broken



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down to its elemental form, ionized, and heated to a temperature of 15,000°K, depending on the gas conditions. This spot of plasma grows outside the laser focus for a high energy laser pulse, with dimensions typically on the order of 10 μm growing to several millimeters, depending on the focal spot size and laser pulse energy.

The atoms and ions in the spark are excited to higher electronic states, causing a very intense pin-point of light to be emitted. Spectral analysis of the ultraviolet and visible emission from the spark using a small spectrograph and time-gated, intensified diode-array detector vields information about the elemental composition of the gas and particles in the spark. Obtaining accurate measurements when the gas and optical conditions change is a major concern in this application of LIBS. Sensitivity and calibration of the optical emission signal may change when the gas and optical conditions change.

To correct for this. Laser Diagnostics developed a proprietary re-calibration technique, which was granted patent protection. The technique involves the analysis of emission spectra taken under a specific set of instrumental conditions. The results of the spectral analysis is then used to correct calibration of elemental analysis as gas and optical conditions change. This should allow reliable and accurate measurements for online measurement of toxic metals in the off-gases of an operating facility.

The development was planned for three stages. The first stage was to demonstrate the utility of the technique using a small laboratory off-gas simulator that allows gas conditions to be varied in a controlled manner. The required spectral analysis was performed using a semi-automated method, requiring some manual correction of the emission calibration.

In the planned second stage of development, a computer program was to be written and optimized for performance of the spectral analysis during data acquisition with realtime re-calibration of LIBS signals. In the third and final stage of development, a working prototype including the re-calibration software was to be demonstrated at a working thermal treatment facility.

Project Conclusion:

This project concluded in September 1997 at the end of the base contract performance period. At completion, the sensor and calibration method had been demonstrated in a environment. laboratory To determine whether this project should continue beyond its base contract period, review of progress was made by four experts (from the Characterization, Monitoring, and Sensor Technology (CMST) Crosscutting Area, the Mixed Waste Focus Area (MWFA), FETC, and an outside expert) in the field of LIBS, and, as a result, additional laboratory testing was conducted to provide additional data on which to make a

more informed decision. The same four experts reviewed the additional progress and provided comments.

FETC determined that progress did not warrant exercising a contract option to continue development.

Contacts:

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